

10/531804

JC12 Doc'd PCT/PTC 18 APR 2005

"Express Mail" mailing label number
EL 2656 98391 US

Date of Deposit April 18, 2005

PATENT
Our Case No. 9378/191

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

INVENTOR:

Eric Girvan Roche
David Alan Stuart
Ernest Philip Grazier
Houyuan Liu

TITLE:

PRODUCTION OF TITANIA

ASSIGNEE:

BHP Billiton Innovation Pty. Ltd.

ATTORNEY:

G. Peter Nichols
BRINKS HOFER
GILSON & LIONE
P.O. BOX 10395
CHICAGO, ILLINOIS 60610

PRODUCTION OF TITANIA

The present invention relates to a process for producing titania from a titaniferous material.

5

The term "titaniferous" material is understood herein to mean any titanium-containing material, including by way of example ores, ore concentrates, and titaniferous slags.

10

The present invention relates particularly to the sulfate process for producing titania from titaniferous material.

15

The sulfate process was the first commercial process for the manufacture of titania from titaniferous ores, such as ilmenite.

20

A significant issue with the sulfate process is that it produces large quantities of waste iron sulfate and consumes large quantities of sulfuric acid.

25

The chloride process generally avoids the iron sulfate waste problem of the sulfate process and, at larger scales, is less expensive to operate than the sulfate process.

30

Hence, the chloride process is the currently preferred process for producing titania, particularly titania for the pigment industry.

An object of the present invention is to provide an improved sulfate process.

35

In general terms, the present invention provides a sulfate process for producing titania from a titaniferous material (such as ilmenite) which includes

includes the steps of:

5 (a) leaching the solid titaniferous material with a leach solution containing sulfuric acid and forming a leach liquor that includes an acidic solution of titanyl sulfate ($TiOSO_4$) and iron sulfate ($FeSO_4$);

10 (b) separating the leach liquor and a residual solid phase from the leach step (a);

(c) separating titanyl sulfate from the leach liquor from step (b);

15 (d) hydrolysing the separated titanyl sulfate and forming a selected particle size distribution of hydrated titanium oxides from titanyl sulfate;

20 (e) separating the solid phase containing hydrated titanium oxides and a liquid phase that are produced in the hydrolysis step (d); and

(f) calcining the solid phase from step (e) and forming titania.

25 The term "hydrated titanium oxides" is understood herein to include, by way of example, compounds that have the formula $TiO_2 \cdot 2H_2O$ and $TiO_2 \cdot H_2O$.

30 In addition, the term "hydrated titanium oxides" is understood herein to include compounds that are described in technical literature as titanium hydroxide ($Ti(OH)_4$).

35 The above-described process is characterised by forming, and more particularly controlling the process so that it is possible to form, the above-mentioned selected particle size distribution of hydrated titanium oxides in

the hydrolysis step (d).

Preferably the process includes controlling the hydrolysis step (d) to produce the selected particle size
5 distribution of the hydrated titanium oxides product.

The process may include controlling the hydrolysis step (d) to produce coarse hydrated titanium oxides, ie oxides having a particle size of at least
10 0.005-0.01mm (ie 5-10 micron).

The controlled growth of coarse particles of hydrated titanium oxides in the hydrolysis step (d) is a significant departure from the conventional sulfate
15 process in which there is a strong preference for producing fine particles in order to produce fine titania that meets the needs of the pigment industry, the major user of titania.

20 There are applications, such as electrochemical reduction of titania, in which it is preferable to have a coarse feed of hydrated titanium oxides or a coarse feed of titania.

25 Alternatively, the process may include controlling the hydrolysis step (d) to produce fine hydrated titanium oxides, ie oxides having a particle size of less than 0.0003 mm (ie 0.3 micron).

30 There are other applications, such as production of pigments, in which it is preferable to have a fine feed of hydrated titanium oxides or a fine feed of titania.

One important parameter for controlling crystal
35 growth is the concentration of titanium in solution within reactor 11. Specifically, it is preferred that the concentration be relatively low, of the order of 10 g/l,

within reactor 11 to achieve growth rather than nucleation of titanium oxide particles.

5 Preferably the process includes a further leach step of leaching the residual solid phase from step (b) with a leach solution containing sulfuric acid and forming a leach liquor that includes an acidic solution of titanyl sulfate and iron sulfate and a residual solid phase.

10 Preferably the further leach step includes separating the leach liquor and the residual solid phase from the further leach step.

15 Preferably the further leach step includes supplying the separated leach liquor to the leach step (a) and/or mixing the separated leach liquor with the leach liquor from step (b).

20 The leach step (a) and the further leach step may be carried out in the same vessel.

25 In that event, the further leach step includes returning the residual solid phase from step (b) to the vessel, wherein the residual solid phase forms part of the titaniferous material subjected to leaching in step (a).

30 Alternatively, the leach step (a) and the further leach step may be carried out in separate, with the residual solid phase from step (b) being supplied to the vessel or vessels for the further leach step.

In that event, preferably the process includes separating the leach liquor and a further residual solid phase formed in the further leach step.

35 The separated leach liquor may be supplied to the leach step (a).

Alternatively, the separated leach liquor may be mixed with the leach liquor from step (b) and thereafter the mixed leach liquor may be processed in the subsequent 5 steps of the process.

The leach step (a) and/or the further leach step may be carried out on a continuous basis or a batch basis.

10 The applicant has found in experimental work that it is important to carry out the leach step (a) and/or the further leach step under leach conditions, described herein, that avoid an undesirable amount of premature hydrolysis of hydrated titanium oxides.

15 In addition, the applicant has found in experimental work that it is important to carry out the leach step (a) and/or the further leach step under leach conditions that avoid an undesirable amount of premature 20 precipitation of titanyl sulfate.

25 Preferably the leach step (a) and/or the further leach step include selecting and/or controlling the leach conditions in the leach step (a) and/or the further leach step to avoid undesirable amounts of premature hydrolysis of hydrated titanium oxides and undesirable amounts of premature precipitation of titanyl sulfate.

30 The relevant leach conditions include any one or more than one of acid concentration, leach temperature and leach time.

35 Typically, the acid concentration in the leach step (a) and/or the further leach step should be at least 350 g/l sulfuric acid throughout the leach step (a) and/or the further leach step when operating at a leach temperature in the range of 95°C to the boiling point in

order to avoid premature hydrolysis.

Typically, the acid concentration at the end of the leach step (a) and/or the further leach step should be less than 450 g/l when operating at a leach temperature in the range of 95°C to the boiling point in order to avoid an undesirable amount of premature precipitation of titanyl sulfate.

It is noted that the acid concentration at the start of the leach step could be higher, typically as high as 700 g/l.

Typically, the leach conditions should be selected and/or controlled so that the titanium ion concentration in the leach liquor is less than 50 g/l in the leach liquor at the end of the leach step (a) and/or the further leach step.

Preferably the titanium ion concentration in the leach liquor is 40-50 g/l.

Preferably the process includes carrying out the leach step (a) in the presence of an additive that accelerates the rate of leaching the titaniferous material.

Preferably the process includes carrying out the further leach step in the presence of an additive that accelerates the rate of leaching the titaniferous material.

The use of the leaching accelerator makes it possible to use less concentrated sulfuric acid than is required for the conventional sulfate process.

Preferably the leaching accelerator is selected

from a group that includes iron, a titanium (III) salt, a thiosulfate salt, sulfur dioxide or any other reduced sulfur containing species.

5 Preferably the process includes carrying out the leach step (a) in the presence of a reductant that reduces ferric ions to ferrous ions in the acidic solution of titanyl sulfate and iron sulfate produced in the leach step (a).

10 Preferably the process includes carrying out the further leach step in the presence of a reductant that reduces ferric ions to ferrous ions in the acidic solution of titanyl sulfate and iron sulfate produced in the leach 15 step (a).

The reductant may be any suitable reductant.

20 Preferably the reductant is selected from a group that includes iron, a titanium (III) salt, a thiosulfate salt, sulfur dioxide or any other reduced sulfur containing species.

25 As is indicated above, the purpose of the reductant is to minimise the amount of iron in the trivalent ferric form and to maximise the amount of iron in the divalent ferrous form in the leach liquor produced in the leach step (a) and/or the further leach step. Maximising the amount of iron in the divalent ferrous form 30 minimises the equilibrium concentrations of iron in the circuit, by promoting the precipitation of ferrous sulfate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

35 Preferably the process includes the steps of precipitating iron sulfate from the leach liquor from step (b) and separating precipitated iron sulfate from the leach liquor prior to the titanyl sulfate separation step

(c).

Preferably the process includes using at least part of the leach liquor remaining after separation of 5 titanyl sulfate in step (c) as at least part of the leach solution in the leach step (a) and/or in the further leach step.

The use of the depleted leach liquor from the 10 titanyl sulfate separation step (c) as the leach solution for leach step (a) and/or the further leach step is an advantage of the process because it maximises the effective use of acid in the process.

15 Preferably the titanyl sulfate separation step (c) includes a solvent extraction step of extracting titanyl sulfate from the leach liquor from step (b) into a solvent and thereafter stripping titanyl sulfate from the solvent and forming a solution that contains titanyl 20 sulfate and thereafter hydrolysing the titanyl sulfate-containing solution in the hydrolysis step (d).

In a situation in which the titanyl sulfate separation step (c) is a solvent extraction step, 25 preferably the process includes using at least part of a raffinate from the solvent extraction step as at least part of the leach solution in leach step (a) and/or in the further leach step.

30 Preferably the leach solution in the leach step (a) and the further leach step includes the raffinate and make-up fresh sulfuric acid.

35 Preferably the raffinate from the solvent extraction step has an acid concentration of at least 250 g/l sulfuric acid.

Preferably the raffinate from the solvent extraction step has an acid concentration of at least 350 g/l sulfuric acid.

5 Preferably the solvent extraction step includes contacting the leach liquor from step (b) with the solvent including a modifier.

10 The term "solvent" is understood herein to mean a reagent and a diluent in combination.

15 The term "modifier" is understood herein to mean a chemical which changes the solubilising properties of the solvent such that the titanium containing species are soluble in the solvent at higher concentrations than might otherwise be possible.

20 Preferably the process includes using the liquid phase produced in hydrolysis step (d) as a source of acid or water in other steps of the process. Typically, the liquid phase includes 100-500 g/l sulfuric acid. By way of example, the liquid phase may be used as a source of acid (and titanium values) by direct addition to leach liquor, depleted leach liquor or any one of steps (a) and 25 (b) and the further leach step. By way of further example, the liquid phase may be used as a source of water for washing solid products from any one of steps (b) and (e).

30 Alternatively, the process may include treating the liquid phase produced in hydrolysis step (d) by neutralising the acid in the liquid phase with lime (CaO) and/or limestone (CaCO₃) and producing clean gypsum (CaSO₄.2H₂O).

35 It is known to produce gypsum by neutralising sulfuric acid in the liquid phase of the hydrolysis step

in the conventional sulfate process. However, the gypsum product includes levels of impurities that reduce the market value of the gypsum. The liquid phase produced in hydrolysis step (d) also includes sulfuric acid that can
5 be neutralised to produce gypsum. However, advantageously, this liquid phase is relatively free of contaminants because the titanyl sulfate precipitation step does not recover substantial amounts (if any) of species (such as iron, chromium, manganese, and niobium)
10 that are in solution in the leach liquor that could act as contaminants. Therefore, gypsum produced from this leach liquor is relatively pure.

Preferably the process includes separating a
15 bleed stream of the leach liquor to minimise the build-up of species (such as vanadium, chromium, and niobium) in solution in the leach liquor.

The above-described process may be carried out as
20 a continuous process or as a batch process.

Preferably the titaniferous material is ilmenite or altered ilmenite.

According to the present invention there is also provided hydrated titanium oxides that have been produced by leaching a titaniferous material (such as ilmenite) with sulfuric acid and forming a leach liquor that includes an acidic solution of titanyl sulfate and iron
25 sulfate and thereafter hydrolysing titanyl sulfate and is characterised in that the hydrated titanium oxides include coarse particles of at least 0.005 mm (5 micron).
30

The process of the present invention includes the following typical reactions.
35

Leaching:

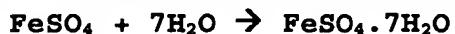


Ferric reduction:



5

Ferrous sulfate crystallisation:



Solvent extraction loading:



Solvent extraction strip:



15

Hydrolysis:



Calcination:



20

The improved sulfate process of the present invention is described further with reference to the accompanying drawings, of which:

25

Figure 1 is a flow sheet that illustrates one embodiment of the process of the invention; and

Figure 2 is a flow sheet that illustrates one embodiment of the process of the invention.

30

With reference to the flow sheet of Figure 1, in a Stage 1 Leach step ilmenite, leach liquor containing between 400 and 700 g/l sulfuric acid from a Stage 2 Leach step, and a reductant in the form of scrap iron are supplied to a digester 3. The process operates on a continuous basis with the feed materials being supplied continuously to the digester 3 and reacted and unreacted

35

materials being discharged continuously from the digester 3.

The Stage 1 Leach step solubilises a substantial component of the ilmenite supplied to the digester 3 and produces a leach liquor that contains titanyl sulfate and iron sulfate. Typically, at the end of the leach the leach liquor contains 20-100 and preferably 40-50 g/l titanium and 50-100 g/l iron.

10

The leach liquor and partially and unreacted ilmenite that are discharged continuously from the digester 3 are subjected to a solid/liquid separation step.

15

The solid phase from the solid/liquid separation step, which contains unreacted and partially reacted ilmenite, is transferred to the Stage 2 Leach step. The Stage 2 Leach step is discussed further below.

20

The leach liquor from the solid/liquid separation step is transferred via a heat exchanger 5a to an iron sulfate crystallisation reactor 7.

25

The heat exchanger 5a cools the leach liquor from a temperature of the order of 110°C to 60°C. The heat extracted by the heat exchanger 5a is used elsewhere in the process, as discussed further below.

30

The leach liquor is cooled further, typically to 10-30°C in the iron sulfate crystallisation reactor 7. Cooling the leach liquor precipitates iron sulfate from the leach liquor in the iron sulfate crystallisation reactor 7. Typically, the crystallisation step reduces the concentration of iron in the leach liquor to 40-50 g/l.

The leach liquor containing precipitated iron sulfate that is discharged from the crystallisation reactor 7 is subjected to a further solid/liquid separation step which separates the precipitated iron sulfate from the leach liquor.

5 The solid phase from the solid/liquid separation step contains iron sulfate. The solid phase may also contain some species such as iron, manganese and
10 aluminium. The solid phase is a by-product of the process.

15 The leach liquor from the solid/liquid separation step is transferred via a heat exchanger 5b to a solvent extraction reactor 9 and contacts a suitable solvent that extracts titanyl sulfate from the leach liquor. Typically, the leach liquor from the solid/liquid separation step is at a temperature of the order of 30°C and the heat exchanger 5b heats the leach liquor to a
20 higher temperature, typically 50°C. Conveniently, the heat input for heat exchanger 5b is heat recovered from the leach liquor by heat exchanger 5a.

25 Suitable solvents are disclosed in Solex US patent 5277816. The solvents include trioctylphosphine oxide and butyl dibutylphosphonate. The present invention is not confined to these extractants.

30 The solvent is used in conjunction with a modifier in the solvent extraction step. Suitable modifiers include methyl isobutyl ketone (MIBK), di-isobutyl ketone (DIBK) and isotridecanol (ITA).

35 The solvent/titanyl sulfate mixture is separated from the leach liquor, and thereafter the titanyl sulfate is stripped from the solvent by water.

The recovered solvent is returned to the solvent extraction reactor 9.

5 The resultant aqueous solution of titanyl sulfate, which typically includes 10-100 g/l titanium in solution and 50-200 g/l sulfuric acid, is transferred to an hydrolysis reactor 11.

10 At start-up, the reactor 11 contains a starting solution of sulfuric acid and solids. Typically, the solution contains 10-200 g/l acid and solids density of 10-200 g/l.

15 The titanyl sulfate solution is added at a controlled rate to the starting solution. The addition of the solution results in the reactor filling up to capacity and thereafter overflowing, whereafter the rate of overflow from the reactor 11 matches the rate of supply of titanyl sulfate solution.

20 In the reactor 11 the sulfate ions in the titanyl sulfate solution are displaced by hydroxyl ions, with the result that hydrated titanium oxides precipitate from the solution.

25 The solids in the starting solution act as seed for precipitation. Typically, the solids are hydrated titanium oxide or titanium dioxide particles.

30 Typically, the residence time of titanyl sulfate solution in the reactor 11 varies between 3 and 12 hours.

35 Subject to temperature and time conditions and control of solution concentration, there is controlled crystal growth in the hydrolysis reactor 11. Controlled crystal growth provides an opportunity to produce titania that ranges from fine to coarse particle sizes. In

particular, controlled crystal growth provides an opportunity to produce coarse titania of greater than 0.005 mm (5 micron) which can be used by way of example in the electrochemical reduction of titania to produce 5 titanium.

The hydrolysis reactor 11 may be operated in batch mode. More preferably, the reactor is operated in continuous mode.

10 Moreover, if required, make-up water and solids can be added to the reactor 11.

15 The overflow from the reactor 11 is collected as the product of the reactor 11.

The product from the hydrolysis reactor 11 is subjected to a solid/liquid separation step, which is facilitated by providing wash water.

20 The solid phase from the solid/liquid separation step, which contains hydrated titanium oxides, is transferred to a calciner (not shown) and is calcined to produce titania. Depending on the circumstances, the 25 solid phase may be calcined at 1000°C to produce titania.

In view of the efficiency of the solvent extraction step in confining extraction substantially to titanium compounds, typically, the process produces 30 titania of very high purity, ie at least 99 wt.%.

Part or all of the liquid phase from the solid/liquid separation step may be reused in the process, for example as a source of acid in the Stage 2 Leach step 35 and/or as a source of water in washing steps in the process, as permitted by the overall water balance.

Alternatively, the liquid phase from the solid/liquid separation step, which contains sulfuric acid, is neutralised with lime and/or limestone and thereby produces a gypsum product. In view of the 5 efficiency of the solvent extraction step in confining extraction to titanium compounds, the liquid phase contains minimal levels of contaminants (such as iron, vanadium and chromium) and therefore the gypsum is "clean" 10 gypsum that is commercially valuable in applications (such as the manufacture of cement).

The raffinate from the solvent extraction step 9 contains relatively high levels of sulfuric acid (250-700 g/l). The raffinate is transferred to the above-mentioned 15 Stage 2 Leach step and is used as a leach liquor. In effect, the solvent extraction step recovers sulfuric acid and the acid can be used productively in the process. This enables a substantial reduction in waste when compared with the conventional sulfate process. In 20 addition, the use of the raffinate as part of the acid feed for the process reduces the amount of fresh acid that is required in the process.

The Stage 2 Leach step is carried out in a 25 digester 13.

The raffinate, and make-up concentrated sulfuric acid that is also supplied to the digester 13, leach the unreacted and partially reacted ilmenite from the Stage 1 30 Leach and solubilise approximately 50% of the remaining ilmenite. The raffinate may be preheated using a heat exchanger 5c before being supplied to the digester 13.

The product from the Stage 2 Leach is subjected 35 to a solid/liquid separation step.

The leach liquor from the solid/liquid separation

step, which typically contains 400-700 g/l sulfuric acid, is transferred to the Stage 1 Leach, as mentioned above.

The solid phase from the solid/liquid separation
5 step is substantially made up of silicate residue, and is a waste product of the process.

Make-up acid is required for the process since there are acid losses in the separation of iron sulfate
10 from the leach liquor and in the extraction of titanyl sulfate in the solvent extraction step.

The make-up acid may be added at any point in the flow sheet.

15 The addition of the acid in the Stage 2 Leach step is a preferred addition point because it is thought that the introduction of concentrated acid at this point optimises the opportunity to leach ilmenite, and it is
20 beneficial to maintaining an efficient heat balance.

The flow sheet of Figure 2 is very similar to that shown in Figure 1 and the same reference numerals are used to describe the same features in both flow sheets.

25 The main difference between the flow sheets is that, whilst the Figure 1 flow sheet describes that the raffinate from the solvent extraction step 9 is transferred to the Stage 2 Leach step and is used as a leach solution in that step, in the Figure 2 flow sheet the raffinate from the solvent extraction step 9 is split into 2 separate streams and is transferred via the separate streams to the Stage 1 Leach step and the Stage 2 Leach step, respectively, and is used as a leach solution
30 in both steps. In addition, whilst the Figure 1 flow sheet describes that the liquid phase of the product from the Stage 2 Leach step is transferred to the Stage 1 Leach

step, in the Figure 2 embodiment the liquid phase is transferred to the leach liquor produced in the Stage 1 Leach step.

5 The applicant has carried out experimental work on a laboratory scale and a pilot plant scale in relation to the above-described process.

10 In summary, the applicant has made the following findings in the experimental scale work.

- Fast leaching rates were achieved by leaching ilmenite in the presence of an accelerator, such as scrap iron, sodium thiosulfate, and sulfur dioxide.
- Leach liquors containing up to 100 g/l titanium were produced.
- 20 • The solvent extraction step resulted in a substantial upgrade in purity of titania that was ultimately produced from the titanyl sulfate extracted in the solvent extraction step.
- 25 • The liquor stripped from the solvent in the solvent extraction step contained high levels (at least 30 g/l) titanyl sulfate.
- 30 • Raffinate can be used to leach ilmenite in the initial and the further leach steps with or without make-up acid.
- 35 • Two stage leaching is an effective leaching option, and the two (or more than two) stage leaching can be carried out in a single vessel with return of residual solid phase to the vessel and addition of fresh ilmenite or in

multiple vessels with the residual solid phase produced in a 1st vessel being supplied to one or more than one other vessel.

- 5 • There is a leach window (that is dependent on conditions such as acid concentration, leach temperature, and leach time and factors such as titanium ion concentration) in which it is possible to avoid premature hydrolysis of
10 hydrated titanium oxides and premature precipitation of titanyl sulfate.

The laboratory scale and pilot plant scale work included leaching samples of heavy mineral sands
15 concentrates containing >50% ilmenite.

The leaching work included leaching work on a batch basis in 2 stages at atmospheric pressure with 30-50% w/w sulfuric acid at 95-120°C for 3-5 hours in each
20 stage, and with additions of accelerator/reductant in the form of iron, sodium thiosulfate and sulfur dioxide in each stage.

The above leaching work was carried out with
25 initial solids loadings of 500 g/l and 200g/l.

Table 1 is a summary of results of the above leaching work.

30 Table 1

Solids loading (in Stage 1)	After Stage 1	After Stage 2
500 g/l	72%	87%
200 g/l	63%	82%

Table 1 indicates that 2 stage leaching, under the conditions described above, is an effective leaching option.

5 The laboratory scale and the pilot plant scale work also included solvent extraction tests on leached ilmenite samples using a range of solvent extraction reagents and modifiers, including reagents of the type disclosed in the US patent 5277816 in the name of Solex
10 Research Corporation of Japan.

The solvent extraction tests were carried out after crystallisation of excess iron sulfate.

15 The reagents included, by way of example, Cyanex 923 [(C₈H₁₇)₃PO equivalent] and the aliphatic diluent Shellsol D100A. The modifiers included, by way of example, methyl isobutyl ketone (MIBK), di-isobutyl ketone (DIBK) and isotridecanol (ITA).

20 Table 2 provides the composition of the feed solution and Table 3 provides titanium enrichment factors in the loaded organic.

25 Table 2

Ti	84 g/l	Ni	28 ppm
Fe	66 g/l	Si	8 ppm
Mn	2.2 g/l	Ca	42 ppm
Cr	87 ppm	Mg	300 ppm
V	270 ppm	Zn	66 ppm

Table 3

	C923	Mix 1	Mix 2	Mix 3	Mix 4
--	------	-------	-------	-------	-------

Ti:Fe	275	450	407	909	1636
Ti:Mn	~inf.	~inf.	~inf.	~inf.	~inf.
Ti:Cr	~inf.	~inf.	~inf.	~inf.	~inf.
Ti:V	4.2	6.0	4.1	4.9	6.1
Ti:Ni	1.4	~inf.	~inf.	~inf.	~inf.
Ti:Si	0.14	~inf.	~inf.	~inf.	~inf.
Ti:Ca	~inf.	0.7	0.1	~inf.	~inf.
Ti:Mg	11	~inf.	~inf.	~inf.	~inf.
Ti:Zn	0.3	~inf.	1.4	2.9	1.3
Ti (g/l)	9.1	15.0	14.0	20.0	9.0

Table 2 indicates that solvent extraction, under the conditions described above, is an effective means of separating titanium (in the form of titanyl sulfate) from contaminants.

The above solvent extraction tests also indicated that solvent extraction is far more effective if a modifier is present. The modifier did not appear to have any effect on the degree of extraction of titanium. However, the modifier appeared to prevent the formation of an undesirable titanium-loaded phase that is not soluble in the diluent. Thus, without the modifier, only relatively dilute solutions of titanium are possible.

15

The following Examples illustrate further the laboratory scale and pilot plant scale work carried out by the applicant.

20 Example 1 - Batch 1st Stage Leach at Constant Acidity

1000 mL of raffinate containing 402 g/l free H₂SO₄, 24.6 g/l Fe²⁺, 2.0 g/l Fe³⁺ and 3.3 g/l Ti was

preheated to 110°C, in a glass reactor equipped with baffles and a Teflon agitator. 400 g of ilmenite, containing 30.4% Ti and 34.3% Fe and ground to 50% passing 32 μ m, was added to this solution with sufficient agitation
5 to fully suspend the solids. A 6mm mild steel rod was immersed into the slurry at a rate of 0.5 cm/hour. Leaching was carried out for 6 hours. Aliquots of 98% sulfuric acid were added throughout to control the free acidity to 400 g/l. After 6 hours a sample was withdrawn
10 and filtered. Analysis of the solution showed it to contain 397 g/l free H₂SO₄, 72.6 g/l Fe²⁺, 3.0 g/l Fe³⁺ and 28 g/l Ti. The slurry was filtered, and the solids washed with water and dried. 252.2 g of residue were obtained in this way, containing 31.9% Ti and 32.7% Fe.

15

Example 2 - Batch Two Stage Leach at Constant Acidity

1000 mL of synthetic raffinate containing 402 g/l free H₂SO₄ was preheated to 105°C, in a glass reactor
20 equipped with baffles and a Teflon agitator. 400 g of ilmenite, containing 30.4% Ti and 34.3% Fe and ground to 50% passing 32 μ m, was added to this solution with sufficient agitation to fully suspend the solids. 30 g of iron filings was added. Leaching was carried out for 5 hours. Aliquots of 98% sulfuric acid were added
25 throughout to control the free acidity to 400 g/l. After 5 hours a sample was withdrawn and filtered. Analysis of the solution showed it to contain 387 g/l free H₂SO₄, 89.4 g/l Fe²⁺, 0.4 g/l Fe³⁺ and 48 g/l Ti. Heat and agitation
30 were switched off and the slurry allowed to settle overnight. 750 mL of the clarified solution was removed and replaced with an equal volume of fresh synthetic raffinate. Heat and agitation were reinstated, and 30 g of iron filings were added. Leaching was continued at 110°C
35 for 5 hours. Aliquots of 98% sulfuric acid were added throughout to control the free acidity to 400 g/l. After 5 hours a sample was withdrawn and filtered. Analysis of

the solution showed it to contain 373 g/l free H₂SO₄, 106 g/l Fe²⁺, 0.2 g/l Fe³⁺ and 38 g/l Ti. The slurry was filtered, and the solids washed with water and dried. 57.5 g of residue were obtained in this way, containing 5 33.0% Ti and 23.7% Fe.

Example 3 - Batch 1st Stage Leach with Reducing Acidity

1000 mL of acidified raffinate containing 598 g/l 10 free H₂SO₄, 31.3 g/l Fe²⁺, 2.4 g/l Fe³⁺ and 9.2 g/l Ti was preheated to 110°C, in a glass reactor equipped with baffles and a Teflon agitator. 400 g of ilmenite, containing 30.4% Ti and 34.3% Fe and ground to 50% passing 32µm, was added to this solution with sufficient agitation 15 to fully suspend the solids. A 6mm mild steel rod was immersed into the slurry at a rate of 0.5 cm/hour. Leaching was carried out for 6 hours. After 6 hours a sample was withdrawn and filtered. Analysis of the solution showed it to contain 441 g/l free H₂SO₄, 73.7 g/l 20 Fe²⁺, 13.0 g/l Fe³⁺ and 47 g/l Ti. The slurry was filtered, and the solids washed with water and dried. 223.6 g of residue were obtained in this way, containing 32.0% Ti and 32.8% Fe.

25 **Example 4 - Batch 2nd Stage Leach with Reducing Acidity**

1000 mL of synthetic raffinate containing 593 g/l free H₂SO₄, was preheated to 105°C, in a glass reactor equipped with baffles and a Teflon agitator. 400 g of 1st 30 stage leach residue, containing 32.0% Ti and 31.3% Fe was added to this solution with sufficient agitation to fully suspend the solids. A 6mm mild steel rod was immersed into the slurry at a rate of 0.5 cm/hour. Leaching was carried out for 6 hours. After 6 hours a sample was withdrawn and 35 filtered. Analysis of the solution showed it to contain 476 g/l free H₂SO₄, 29.0 g/l Fe²⁺, 10.4 g/l Fe³⁺ and 32.5 g/l Ti. The slurry was filtered, and the solids washed

with water and dried. 267 g of residue were obtained in this way, containing 31.9% Ti and 30.7% Fe.

Example 5 - Pilot Plant 1st Stage Leach with Reducing
5 Acidity

39 L of 98% sulfuric acid was added to 243 L of raffinate containing 358 g/l free H₂SO₄ and 7 g/l Ti, in a fibre reinforced plastic (FRP) tank of 300 L capacity,
10 equipped with a FRP axial turbine. The resulting solution, which contained 579 g/l free acid, 27.9 g/l Fe²⁺ and 5.6 g/l Fe³⁺, was preheated to 95°C. 116 kg of unground ilmenite, containing 31.1% Ti and 34.1% Fe was added to this solution with sufficient agitation to fully suspend
15 the solids. A group of ten 10mm mild steel rods of length 29 cm was immersed into the slurry. Leaching was carried out for 6 hours at 105°C. The slurry was filtered using a pressure filter, to produce approximately 260 L of solution. Analysis of the solution showed it to contain
20 461 g/l free H₂SO₄, 72.6 g/l Fe²⁺, 9.0 g/l Fe³⁺ and 41 g/l Ti.

Example 6 - Pilot Plant 1st Stage Leach with Constant
Acidity

25 A single stage leach pilot plant was assembled, consisting of 5 stirred FRP tanks of 10 L capacity each, equipped with FRP double axial turbines, and silica jacketed electric immersion heaters. Ilmenite ground to 50% passing 32µm was fed to the first tank at 750 g/hour using a screw feeder. SX pilot plant raffinate of composition 404 g/l free H₂SO₄, 36.1 g/l Fe²⁺, 3.2 g/l Fe³⁺ and 10 g/l Ti, was also pumped into the first tank at a rate of 62.5 mL/min. The temperature was maintained at
30 110°C in all tanks. 98% sulfuric acid was added to the first two tanks to control the acidity to 400 g/l. Mild steel rods of diameter 10mm were inserted into each tank
35

at a rate of 1cm/hr. Slurry was thence allowed to flow by gravity to a FRP thickener equipped with FRP rakes. Thickener overflow solution and underflow slurry were collected and stored. The pilot plant was operated 5 continuously for 92 hours. During the final 48 hours of operation the average composition of the solution in each tank was as set out below in Table 4.

Table 4: Continuous Pilot Plant 1st Stage Leach Results

10

	Free Acid g/l	Fe ²⁺ g/l	Fe ³⁺ G/l	Ti g/l
Tank 1	411	48	2.7	16
Tank 2	404	56	2.5	20
Tank 3	402	65	2.4	29
Tank 4	395	68	4.2	36
Tank 5	391	65	6.1	34
Thickener overflow	388	70	3.0	33

Example 7: SX Bench Tests with Counter-current Extraction:

15 Three groups of counter-current bench tests were carried out to simulate the SX extraction circuit of the pilot plant operation. Each group involved 5 cycles and the data indicated that a steady state was achieved. The organic phase contained 30%vol Cyanex 923 as the extractant, 5%vol DIBK as the modifier and 65%vol Shellsol D100A as the diluent. At the O/A ratio of 2, 3 and 4, the organic loading was 16, 11 and 8 g/l Ti, the extraction efficiency was 97.8, 99.7 and 99.9%; the titanium concentrations of raffinate were 450-910, 80-120 and 24-28 mg/l respectively. The separation between Ti and Cr, Mg, Mn, Ni approached perfect with the loaded organic

20

25

containing 0 mg/l of Cr, Mg, Mn and Ni. The test was carried out on flask shaker in an incubator. The major test conditions are shown as follows:

5 Temperature: 50° C
 Mixing time: 45-60 minutes
 Settling time: 15 minutes
 O/A ratio: 2, 3, 4

10 The results are summarised in Table 5.

Table 5: Composition of Organic, Feed and Raffinate at Given O/A Ratio (mg/l)

		H ₂ SO ₄	Ca	Cr	Fe	Mg	Mn	Ni	P	Si	Ti	Y	Zn
Feed		441000	10	52	39000	220	1400	7	0	27	32000	120	47
O/A	Org	28000	4	0	708	0	0	0	20200	6	15600	13	0
2	Raf	327000	14	55	37200	222	1500	9	0	76	676	108	47
O/A	Org	23000	1	0	1920	0	0	0	20200	5	11000	12	6
3	Raf	314000	14	55	34800	224	1540	9	4	3	89	106	48
O/A	Org	22000	2	1	2160	0	0	1	20000	4	8360	10	0
4	Raf	296000	15	58	34600	240	1600	10	7	6	25	100	51

15

Example 8: SX Bench Stripping Test

20 The loaded organic that contained 30%vol Cyanex 923 as the extractant, 5%vol DIBK as the modifier and 65%vol Shellsol D100A as the diluent was stripped with water with various O/A ratio. The test was carried out using a flask shaker in an incubator. The major test conditions are shown as follows:

25 Temperature: 50°C
 Mixing time: 60 minutes
 Settling time: 20 minutes
 O/A ratio: 1/3, 1/1, 3/1,
 5:/1, 10/1, 20/1

and 30/1

The results are summarised in Table 6.

5 Table 6: Composition of Organic and Stripping Solution at Given O/A Ratio (mg/l)

		H ₂ SO ₄	Ca	Cr	Fe	Mg	Mn	Ni	P	Si	Tl	Y	Zn
Loaded Organic		n.a	13	0	44	3	0	0	20000	4	18000	12	8
O/A	Org	n.a	14	0	47	3	0	0	21000	5	3400	8	19
	Strip	14700	2	0	16	0	0	0	6	0	3800	3	0
O/A	Org	n.a	14	0	18	0	0	0	20000	6	11000	12	10
	Strip	44100	2	37	0	0	0	0	7	0	7200	6	1
O/A	Org	n.a	12	0	16	0	0	0	20000	5	15000	13	9
	Strip	103000	2	0	97	0	0	0	7	0	8000	7	2
O/A	Org	n.a	13	0	30	4	0	0	20000	4	16000	17	25
	Strip	156900	0	0	160	0	0	0	3	0	7200	7	0
O/A	Org	n.a	3	0	26	3	0	0	20000	0	17000	18	20
	Strip	225600	2	0	280	0	0	0	0	0	5800	6	3
O/A	Org	n.a	0	0	40	2	0	0	20000	0	17000	17	20
	Strip	343000	4	0	490	0	0	0	0	1	4700	8	0
O/A	Org	n.a	10	0	41	0	0	0	19000	0	17000	15	6
	Strip	392300	2	1	710	0	0	0	0	0	4500	7	2

*: White precipitation formed in both organic and aqueous phase

10

Example 9: SX Pilot Plant Operation

15 The pilot plant operation was carried out with a device that involved two extraction cells, one scrub cell and four stripping cells. The effective volume of mixer and settler of each cell were 1.675 and 8.000 liter respectively. The stripping involved two stages: the lead strip with hydrolysis thickener overflow and lag

stripping with water respectively. The major operational conditional were as follows:

Temperature: 50 °C

5 Organic Composition: 25%v/v Cyanex 923, 5%v/v Iso-tri-decanol and 70%v/v ShellSol D100A. The capacity of organic was 15.7 g/l Ti.

10 Feed Composition: 36 g/l Ti, 410 g/l H₂SO₄, 47 g/l Fe including 4.0 g/l Fe³⁺

Mixing time: 5-10 minutes

Settling time: 40 minutes

O/A flow ratio of extraction: ~5:1. Organic flow: 165 mL/min;

15 Feed flow: 33 mL/min

O/A flow ratio of scrub: ~10:1.

Org. flow: 165 mL/min;

Aqu. flow: 17 mL/min

20 O/A flow ratio of lead strip: ~4:1.

Org. flow: 165 mL/min;

Aqu. flow: 41 mL/min

O/A flow ratio of lag strip: ~8:1.

Org. flow: 165 mL/min;

25 Aqu. Flow: 21 mL/min

The results are summarised in Table 7.

Table 7: Average Compositions of Aqueous and Organic
30 Liquor

	H ₂ SO ₄ g/l	Ca mg/l	Cr mg/l	Tot. Fe mg/l	Fe ³⁺ mg/l	Mg mg/l	Mn mg/l	Ni mg/l	P mg/l	Si mg/l	Ti mg/l	V mg/l	Zn mg/l
Feed	410	58	43	47000	4000	430	1900	4	22	17	36000	200	41
Raff	345	48	29	30529	5700	319	1371	4	2	10	5324	122	30

Lead Strip	178	27	1	465	465	2	0	0	13	5	11306	16	1
Lag Strip	91	28	2	224	224	3	1	0	15	5	16329	21	1
Loaded Org. (S2)	n.a	3	1	160	160	1	0	0	16647	0	15059	22	2
Strip Org. (S1)	n.a	3	0	23	23	1	0	0	17000	0	7224	11	3

Example 10: Pilot Plant Operation

The pilot plant operation was carried out with a device that involved two extraction cells, one scrub cell and four stripping cells. The effective volume of mixer and settler of each cell were 1.675 and 8.000 liter respectively. The stripping involved two stages: the lead strip with hydrolysis thickener overflow and lag stripping with 50 g/l H₂SO₄ respectively. The major operational conditional were as follows:

Temperature: 50 °C
Organic Composition: 25%v/v Cyanex 923, 5%v/v Iso-tri-decanol and 70%v/v ShellSol D100A. The capacity of organic was 15.7 g/l Ti.
Feed Composition: 36 g/l Ti, 410 g/l H₂SO₄, 47 g/l Fe including 4.0 g/l Fe³⁺
Mixing time: 5-10 minutes
Settling time: 40 minutes
O/A flow ratio of extraction: ~5:1.
Organic flow: 165 mL/min;
Feed flow: 32 mL/min
O/A flow ratio of scrub: ~10:1.
Org. flow: 165 mL/min;

Aqu. flow: 17 mL/min
O/A flow ratio of lead strip: ~4:1.
Org. flow: 165 mL/min;
AQU. flow: 41 mL/min
5 O/A flow ratio of lag strip: ~8:1.
Org. flow: 165 mL/min;
AQU. Flow: 21 mL/min

The results are summarised in Table 8.

10

Table 8 Average Compositions of Aqueous and Organic Liquor

	H ₂ SO ₄ g/l	Ca mg/l	Cr mg/l	Tot. Fe mg/l	Fe ²⁺ mg/l	Mg mg/l	Mn mg/l	Ni mg/l	P mg/l	Si mg/l	Ti mg/l	V mg/l	Zn mg/l
Feed	415	83	45	49000	5200	650	1800	5	17	21	34000	350	30
Raff	363	65	29	29500	5000	360	1258	5	0	11	3950	115	29
Lead Strip	223	53	2	408	408	5	0	0	24	7	17167	28	1
Lag Strip	113	54	1	56	56	6	0	0	7	7	9300	14	1
Loaded Org. (B2)	n.a.	15	1	177	177	0	0	0	19167	2	15917	23	3
Stripp-ed Org.(ST1)	n.a.	2	0	0	0	0	0	0	19750	1	10358	17	0

15 Example 11 - Batch Hydrolysis

1000 mL of SX pilot plant loaded strip liquor containing 123 g/l free H₂SO₄, 0 g/l Fe²⁺, 0.26 g/l Fe³⁺ and 12 g/l Ti was pretreated with 1 g of aluminium foil overnight at room temperature. Titration with dichromate with sodium diphenylamine sulfonate as indicator showed the resulting solution to contain 2.4 g/l Ti³⁺. 500 mL of water containing 100 g/l free H₂SO₄, and 0.5 g of TiO(OH)₂

with sodium diphenylamine sulfonate as indicator showed the resulting solution to contain 2.4 g/l Ti³⁺. 500 mL of water containing 100 g/l free H₂SO₄, and 0.5 g of TiO(OH)₂ seed, was preheated to 95°C, in a glass reactor equipped
5 with baffles and a Teflon agitator. The treated loaded strip liquor was then pumped into the reactor at 2.8 mL/min over 6 hours. The reaction mixture was allowed to stir for a further 30 minutes then a sample was withdrawn and filtered. Analysis of the solution showed it to
10 contain 147 g/l free H₂SO₄, 0.24 g/l Fe and 2.3 g/l Ti. The slurry was filtered, and the solids washed with water and dried. Filtration was found to be very fast. 22.6 g of residue were obtained in this way, containing 45.0% Ti, 3.9% S and <0.02% Fe with d₅₀ particle size approximately
15 8.5 micron.

Example 12 - Pilot Plant Hydrolysis

A single stage hydrolysis pilot plant was
20 assembled, consisting of 2 stirred FRP tanks of 5 L capacity each, equipped with FRP double axial turbines, and silica jacketed electric immersion heaters. SX pilot plant loaded strip liquor containing 206 g/l free H₂SO₄, 0 g/l Fe²⁺, 0.2 g/l Fe³⁺ and 25 g/l Ti, was pumped into the
25 first tank at a rate of 10 mL/min. The temperature was maintained at 95°C in each tank. Water was added to the first tank to control the acidity to 140 g/l, requiring a flow of 8.5 mL/min. Additional water was added to the second tank at 5 mL/min to control the acidity to 100 g/l.
30 Slurry was thence allowed to flow by gravity to a FRP thickener equipped with FRP rakes. Thickener overflow solution was collected and stored. The thickener underflow slurry was collected and filtered by vacuum filtration. Filtration of the underflow was found to be very fast. The
35 d₅₀ particle size was found to be 7.2 micron. The pilot plant was operated continuously for 42 hours. During the final 30 hours of operation the average composition of the

solution in each tank was as follows:

Table 9: Continuous Pilot Plant Hydrolysis Results

	Free Acid g/l	Fe g/l	Ti g/l
Tank 1	136	0.13	4.6
Tank 2	105	0.09	1.0
Thickener overflow	109	0.09	1.0

5

Example 13 - Laboratory Scale Calcination

A 2.6 g sample of dried TiO(OH)_2 , produced according to Example 11 was calcined in an alumina crucible, using a 10 muffle furnace at 1000°C for 1 hour. On removal from the furnace the cooled calcine was found by XRF to contain 59.8% Ti, 0.07% Fe, <0.02% S and less than detection limit for Si, Al, Mn, Mg, Cr, V and Zn.

15 Many modifications may be made to the process of the present invention described above without departing from the spirit and scope of the present invention.

20 By way of example, whilst the above-described flow sheet describes that the Stage 1 and Stage 2 Leach steps are carried out in single digesters 3 and 13, respectively, the present invention is not so limited and extends to arrangements that include multiple digesters for each stage.

25 In addition, whilst the above-described flow sheet describes that the Stage 1 and Stage 2 Leach steps are carried out in separate digesters 3 and 13, respectively, the present invention is not so limited and 30 extends to arrangements in which leaching of titaniferous

material is carried out in a single digester, with return of residual solid phase to the digester and direct supply of raffinate from the solvent extraction step 9 to the digester.